

AIR PRODUCTS AND CHEMICALS, INC. BIO. PROGRAM  
ELKTON PLANT

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# AIR PRODUCTS AND CHEMICALS, INC. BIO. PROGRAM ELKTON PLANT

DATE	SV-1	SV-2A	SV-3A	SV-4	
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11/10/2009	0	0	0	0	
12/8/2009	0	0	0	0	

# AIR PRODUCTS AND CHEMICALS, INC. BIO. PROGRAM ELKTON PLANT

DATE	SV-1	SV-2A	SV-3A	SV-4	
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# AIR PRODUCTS AND CHEMICALS, INC. BIO. PROGRAM ELKTON PLANT

DATE	SV-1	SV-2A	SV-3A	SV-4	
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8/4/2007	0	0	0	0	
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10/15/2007	0	0	0	0	
11/7/2007	0	0	0	0	
12/27/2007	0	0	0	0	

## ELKTON PLANT

### PRSPP MANUAL

Orig. Issue Date February 1993

Procedure No. 50

Last Review Date June 2005

Page 1 of 2

#### SUBJECT: VINYL ACETATE UNDERGROUND LEAK MONITORING

##### 1. PURPOSE

The purpose of this procedure is to establish guidelines for computing and filing the monthly Leak Monitoring Report.

##### 2. RESPONSIBILITY

It is the responsibility of the Lab Technician to complete this report on a monthly basis.

##### 3. STANDARD PROCEDURE FOR LEAK MONITORING OF VINYL ACETATE (VA) TANKS

5.1 Responsibility: The Lab Technician is responsible to perform the below test on a monthly basis.

##### 5.2 Supplies needed:

5.2.1 10 ml gastight syringe with Luer-Lok tip - Qty. 2

5.2.2 24 gauge stainless steel Luer-Lok needles - Qty. 2

5.2.3 1/8 inch OD Teflon tubing - 5 feet

5.2.4 1/8 inch ID Tygon tubing - <1 foot

5.2.5 stainless steel 3-way valve with at least one male and one female Luer-Lok end - Qty. 1

5.2.6 headspace vials with septa and caps - enough for all sampling points

##### 5.3 Procedure

5.3.1 Seal five 22ml headspace vials in the usual manner.

5.3.2 Using a 10ml gastight syringe with 24 gauge needle, puncture septum and withdraw 10ml of air from headspace vial. Repeat this for all vials.

5.3.3 Attach six feet of 1/8" OD Teflon tubing to hose barb end of a 3-way valve using a half inch piece of 1/8" ID Tygon tubing.

5.3.4 Connect a stainless steel Swagelok fitting (for weight) to the other end of Teflon tubing and mark it 5ft from the fitting.

5.3.5 Connect a 10ml gastight syringe to the female Luer-Lok end of 3-way valve. DO NOT OVERTIGHTEN!

5.3.6 Connect a 24 gauge needle to the male Luer-Lok end of 3-way valve.

5.3.7 Unscrew monitor readout from top of well casing and slowly lower it to the ground. REMEMBER TO MINIMIZE DISTURBANCE OF WELL VAPOR.

ELKTON PLANT

PRSPP MANUAL

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SUBJECT: VINYL ACETATE UNDERGROUND LEAK MONITORING

- 5.3.8 Lower Teflon tubing into well until 5ft mark is even with top of the pipe.
- 5.3.9 Loosely stopper top of well so as not to pinch monitor wires or Teflon tubing.
- 5.3.10 Turn 3-way valve so that syringe is open to tubing.
- 5.3.11 Draw 10ml of well air into syringe.
- 5.3.12 Turn 3-way valve so that syringe is open to needle.
- 5.3.13 Push air out of syringe.
- 5.3.14 Return 3-way valve to previous position.
- 5.3.15 Withdraw another 10ml of well air.
- 5.3.16 Open 3-way valve between syringe and needle and insert needle into headspace vial.  
This order is IMPORTANT!
- 5.3.17 SLOWLY dispense contents of syringe into headspace vial and pull needle out of septum.
- 5.3.18 Repeat steps 14-17 for second vial, if necessary.
- 5.3.19 Remove tubing from well and secure well top.
- 5.3.20 Repeat steps 14-17 using outside air to flush equipment.
- 5.3.21 Label vial with well identification. Vial is now ready for analysis.
- 5.3.22 Repeat steps 7 to 21 for each remaining well.
- 5.3.23 Input reading in file server under the below described folder:  
Server: ELMBNT (O:\Admshare\Plteng\USTVapTesting\wellvapor)



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Plant Manager

[illegible]

HEADSPACE CALIBRATION STANDARDS - AF2027									
			673926	Instrument # 3		DATE:	2/4/2010		
<b>Spiked Emulsion</b>						<b>Spiked Emulsion</b>			
<b>Component</b>	<b>Weight (grams)</b>					<b>Component</b>	<b>Weight ppm</b>		
726201	30.0120								
vinyl acetate	0.0420					vinyl acetate	1397.5		
<b>TOTAL</b>	30.0540								
<b>Component</b>	<b>Emulsion Sample Area Counts</b>		<b>Spiked Emulsion Area Counts</b>			<b>Emulsion Sample</b>			
						<b>Component</b>	<b>Weight ppm</b>		
vinyl acetate	1100.9		4275.9			vinyl acetate	484.6		





## Piedmont Plant Standard Operating Procedure

**Procedure:** GC6890 Headspace Injection Calibration Procedure

**Procedure No:** 809.05

**Revision Date:** 29 October 2007

**Author:** Gerald Taylor

**Revision No:** 3

**Approver:** Daniel Glessner

**MOC No.:** 22142

**Personal Protective Equipment Required:** Safety Glasses, Nitrile Gloves

STEP	HAZARD/REASON
1. Obtain samples of PSA emulsion and Hybridur products to perform this calibration. Calibrating using this technique requires that the sample must contain the substance of interest. An example would be that AF2027 contains Vinyl Acetate.	Use standard PPE when handling samples.
2. Weigh 10 grams $\pm$ 0.1 grams of the emulsion into a 20 ml headspace vial. This will be the emulsion sample vial.	Performed under fume hood.
3. Place a plastic bottle capable of holding 30 grams of emulsion on scales.	
4. Add 30 grams of the same emulsion used in step 2 to the plastic bottle. Record weight.	
5. Add three drops of the substance (s) of interest to the plastic bottle Record the weight.	Perform under fume hood.
6. Enter the weights from steps 3 and 4 above into the Individual Component Addition spreadsheet.	The spread sheet calculates the response factor of the substance.
7. Shake sample by hand or use the wrist action shaker until mixed.	
8. Place 10 grams $\pm$ 0.1 grams of the spiked emulsion prepared in steps 4 and 5 above into a 20 ml headspace vial. This is the spiked emulsion sample.	
9. Place the emulsion sample into slot 1 and the spiked emulsion into slot 2 of the headspace sampler.	
10. Choose the appropriate instrument for headspace injection from the Windows menu of the Chemstation Click on METHOD and select LOAD METHOD, Choose the appropriate method for the	

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## Piedmont Plant Standard Operating Procedure

**Procedure:** GC6890 Headspace Injection Calibration Procedure

**Procedure No:** 809.05

**Revision Date:** 29 October 2007

**Author:** Gerald Taylor  
**Approver:** Daniel Glessner

**Revision No:** 3  
**MOC No.:** 22142

**Personal Protective Equipment Required:** Safety Glasses, Nitrile Gloves

analysis. Click on SEQUENCE and select LOAD SEQUENCE. Choose the appropriate sequence. An example is "VAM"	
11. Click on SEQUENCE and select SEQUENCE PARAMETERS. In the subdirectory box enter work std. In the prefix box type in the standard number such as gc2-107.	
12. Click on SEQUENCE and select SEQUENCE TABLE. In the table enter the batch or lot number in sample name box on line 1. Enter SPIKED in the sample name box for line 2. Enter 1 in the SAMPLE AMT, INTERNAL STD AMOUNT, MULTIPLIER, and the INJ VOL boxes on both lines 1 and 2. Click on RUN SEQUENCE	
13. After both samples have run, place the area counts from the emulsion and spiked emulsion chromatograms in the Individual Component Addition spreadsheet to calculate the ppm of the substance in the emulsion sample. For example, if the AF2027 sample is used, the only monomer that will be appear on the emulsion chromatogram will be VAM. The spreadsheet will calculate the ppm VAM from the emulsion chromatogram. The results from the chromatogram of the emulsion should be within $\pm 50$ ppm of the calculated result from the spreadsheet. If the results are not within the calibration tolerance fill out an "OUT OF CALIBRATION" report.	Dispose of the sample vials in the lab garbage.
14. Go into the data analysis section of the Chemstation by clicking on VIEW and selecting DATA ANALYSIS.	
15. Click on CALIBRATION and select CALIBRATION TABLE to display the calibration table.	
16. In the calibration table enter the area counts from the emulsion GC run in the area column of the calibration table. Also enter the ppm amount from the	



## Piedmont Plant Standard Operating Procedure

**Procedure:** GC6890 Headspace Injection Calibration Procedure

**Procedure No:** 809.05

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**MOC No.:** 22142

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Individual Component Addition spreadsheet in the amount ppm column of the calibration table.	
17 Click on VIEW and select METHOD AND RUN CONTROL	
18. Click on METHOD and select SAVE METHOD	

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## ANALYTICAL PROCEDURE

Procedure No. 96-CRSD-125  
Rev. 1  
PAGE 1 OF 18  
EFFECTIVE DATE August 20, 1999

**TITLE:** HEADSPACE GAS CHROMATOGRAPHIC METHOD FOR  
THE ANALYSIS OF RESIDUAL VOLATILE ORGANIC COMPOUNDS  
(VOC) IN WATER-BASED POLYMER EMULSIONS

### I. SCOPE

This is a headspace gas chromatographic method for the quantitative determination of residual volatile organic compounds (VOC) in water-based polymer emulsions and redispersible powders. The components which can be analyzed by this method include, but are not limited to, those listed below. This method is capable of accurately determining concentrations ranging from 1 wt ppm to approximately 5000 wt ppm.

vinyl chloride	acetaldehyde	methanol
pentane	ethanol	acetone
isopropanol	methyl acetate	t-butanol
vinyl acetate	n-propanol	ethyl acetate
methyl acrylate	methyl ethyl ketone	n-heptane
benzene	isobutanol	methyl cyclohexane
n-butanol	n-propyl acetate	1,4-dioxane
toluene	n-butyl acetate	n-butyl acrylate

In addition to the above components, this method is also suitable for the determination of some light hydrocarbons, such as methane, ethane/ethylene, propane/propylene and isobutylene. A number of other components may be present in the sample headspace but will coelute with some of those listed above. These include trans-2-methyl hexene (coeluting with t-butanol), 2-methyl hexane (coeluting with n-propanol), methyl propionate (coeluting with n-heptane), isopropyl acetate (coeluting with benzene), ethyl acrylate (coeluting with n-butanol), crotonaldehyde (coeluting with n-butanol), methyl methacrylate (coeluting with n-propyl acetate) and methyl isobutyl ketone (coeluting with toluene).

This method contains information which is directly applicable for the analysis of specific polymer emulsion products. The primary difference is that the calibration standards are prepared to contain only the specific components of interest in those products. The subsequent calculation of sample composition also includes only these components of interest.

### II. PRINCIPLE

A ten gram aliquot of the sample emulsion is weighed into a headspace vial which is then sealed securely with a Teflon-faced silicone septum and crimp-top aluminum cap. The sealed vial is thermostated for thirty minutes at either 30°C or 40°C, depending on the manufacturer of the headspace unit in use. During the equilibration time the volatile organic compounds are preferentially partitioned into the gaseous headspace of the vial. After equilibration, a one milliliter aliquot of the vial headspace is injected into the carrier gas stream of a gas chromatograph. The sample components are selectively separated on a 60 meter x 0.32 mm ID Restek Rtx-1701 FSOT capillary column having a stationary phase film thickness of 1.5 microns. The detector response (peak area) of each component is proportional to the concentration of that component in the sample.

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Quantitation of the volatile organic compounds in the sample is obtained by using a standard addition technique and/or an external standardization calculation. An absolute detector response factor is determined for each component in the calibration standard. These response factors are then used to calculate the concentration of each component present in the sample.

### III. APPARATUS

#### A. Gas Chromatograph

Implementation of this method requires a gas chromatograph equipped with a flame ionization detector, a split/splitless capillary flash vaporization injector, a temperature-programmable column oven and separately controlled injector and detector temperatures. A Hewlett-Packard Model 5890 Series II gas chromatograph (Hewlett-Packard Corporation, King of Prussia, Pennsylvania) was used for this method.

#### B. Headspace Analyzer

The sample analysis may be automated by using a headspace analyzer, such as a Tekmar Model 7000 Headspace Analyzer (with a Model 7050 Autosampler) or the Hewlett-Packard Model 7694 Headspace Analyzer. Manual analyses may also be performed using a gas-tight syringe although this is considerably more time consuming and the reproducibility and accuracy of the method are decreased.

#### C. Data System

Any data system which is capable of accurately and reproducibly determining the areas and retention times of the eluting components is acceptable for use with this method. A Perkin-Elmer/Nelson Analytical Turbochrom 3 data system was used in the development of this method.

### IV. REAGENTS AND MATERIALS

#### A. Capillary Column

Restek Rtx-1701 FSOT capillary column (60 meter x 0.32 mm ID) with a stationary phase film thickness of 1.5 microns (Catalog Number 12072), Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823-8812, Telephone (814) 353-1300.

#### B. Headspace Vials

For the Tekmar headspace unit, this method requires the use of 22 mL vials (catalog number 14-4440-024) with 20 mm crimp caps (catalog number 14-4436-000) and Teflon-faced silicone septa (catalog number 14-5518-043), available from Tekmar Company, Cincinnati, OH.

For the Hewlett-Packard headspace unit, this method requires the use of 20 mL vials (catalog number 5182-0837) with 20 mm standard crimp caps (catalog number 9301-0721) and Teflon-faced silicone high temperature septa (catalog number 9301-0719), available from Hewlett Packard Corporation, King of Prussia, PA. These items may also be purchased together as a supply kit (catalog number 5182-0840).

C. Chemicals

All chemicals which may be required for the preparation of the standard mixtures described in Section V-F are available from Aldrich Chemical Co., Milwaukee, Wisconsin.

<u>Chemical</u>	<u>CAS Number</u>	<u>Catalog Number</u>
vinyl chloride	75-01-4	38,762-2
acetaldehyde	75-07-0	11,007-8
methanol	67-56-1	27,047-4
pentane	109-66-0	27,041-5
ethanol	64-17-5	27,074-1
acetone	67-64-1	17,912-4
isopropanol	67-63-0	27,049-0
methyl acetate	79-20-9	29,699-6
t-butanol	75-65-0	30,825-0
(2-methyl-2-propanol)		
vinyl acetate	108-05-4	V150-3
n-propanol	71-23-8	29,328-8
ethyl acetate	141-78-6	27,052-0
methyl acrylate	96-33-3	M2,730-1
methyl ethyl ketone	78-93-3	27,069-5
n-heptane	142-82-5	27,051-2
benzene	71-43-2	27,070-9
isobutanol	78-83-1	27,046-6
(2-methyl-1-propanol)		
methyl cyclohexane	108-87-2	25,969-1
n-butanol	71-36-3	27,067-9
n-propyl acetate	109-60-4	13,310-8
1,4-dioxane	123-91-1	27,053-9
toluene	108-88-3	27,037-7
n-butyl acetate	123-86-4	27,068-7
n-butyl acrylate	141-32-2	23,492-3

If the secondary (coeluting) components listed in Section I are of interest, these may also be obtained from Aldrich Chemical Co.

<u>Chemical</u>	<u>CAS Number</u>	<u>Catalog Number</u>
2-methyl hexane	591-76-4	M4,970-4
trans-2-methyl hexene	6094-02-6	11,162-7
(2-methyl-1-hexene)		
methyl propionate	554-12-1	10,925-8
(methyl propanoate)		
isopropyl acetate	108-21-4	18,547-7
ethyl acrylate	140-88-5	E970-6

**V. PROCEDURE****A. Installation and Conditioning of Capillary Column**

The capillary column should be installed in the gas chromatograph according to the instrument manufacturer's instructions. Contamination of the column ends from graphite ferrules must be particularly avoided to prevent adsorption of polar components of the sample. Leak checking of the fittings connecting the column to the injector and detector should be done with a helium gas leak detector, if available, rather than a soap solution to prevent contamination of the column if a leak is present. If proper column installation procedures are followed, the potential for a gas leak is extremely small.

Unless otherwise specified by the column manufacturer, the installed column should be conditioned prior to use by heating the oven to 250°C (the maximum operating temperature of the Restek Rtx-1701 column is 280°C during temperature programming). First ascertain that carrier gas is flowing through the column and that all air has been flushed from the column before heating. The temperature of the oven should be increased at 6°C/minute during the initial conditioning step. Hold the column at the upper temperature of 250°C for one or two hours and then return to the initial temperature.

**B. Gas Chromatograph Operating Parameters**

**Column** Restek Rtx-1701 FSOT capillary, 60 m x 0.32 mm ID, 1.5 micron film thickness

Oven Temperature Program	<u>for vinyl acetate only</u>		<u>for complete VOC</u>	
Initial Temperature	45	°C	45	°C
Initial Time	3	minutes	3	minutes
Program Rate <sup>1</sup>	8	°C/minute	6	°C/minute
Final Temperature <sup>2</sup>	180	°C	180	°C
Final Time <sup>3</sup>	0	minutes	5	minutes
Total Analysis Time <sup>4</sup>	19.9	minutes	30.5	minutes

**Carrier Gas** Helium

Flow Rate <sup>5</sup>	1.8 - 2.2	mL/minute
Column Headpressure <sup>6</sup>	15 - 18	psig
Split Flow Rate	30	mL/minute

**Detector Type** Flame Ionization

Detector Temperature <sup>7</sup>	200	°C
Amplifier / Range Setting <sup>8</sup>	1 - 2	

**Injector Temperature** 150 °C

**Injection Mode** Tekmar Model 7000 Headspace Analyzer with Model 7050 Autosampler or  
Hewlett-Packard 7694 Headspace Analyzer

Notes: <sup>1</sup> The program rate should be decreased from 8 °C/minute to 6 °C/minute to provide better separation between closely eluting components when performing an analysis for complete VOC content.

<sup>2</sup> The final oven temperature should be increased as necessary (maximum of 240 °C) if higher molecular weight components are present in the sample headspace which do not completely elute when using a final temperature of 180 °C.

- ### C. Tekmar Headspace Analyzer Parameters

**Gas Chromatograph Cycle Time<sup>5</sup>**      30 - 40      minutes

- Headspace gas chromatography (HSGC) is a procedure for the determination of volatile constituents which are in thermodynamic equilibrium between the sample and the surrounding vapor phase in a closed system. HSGC is primarily concerned with the determination of trace levels of volatile components in samples which are difficult to analyze by conventional gas chromatographic methods, such as polymer emulsions.



The peak area of a given component analyzed by equilibrium (static) headspace gas chromatography depends on a number of factors, including the sample volume, the partition coefficient of the component between the gas and the liquid/solid phase in the headspace sample vial and the unique response of the detector for that component. Although the relationship used to calculate the detector response factor does not differ from that used for other quantitative methods, it is necessary in HSGC to include the partition coefficient, and thus the matrix, in the calibration procedure.

The absolute detector response factor for each component is usually constant over a fairly wide range of concentrations. It is acceptable in this method, therefore, to determine the response factor at only one concentration.

#### E. Preparation of Emulsion Calibration Standard

An instrument calibration standard, consisting of an emulsion product containing known concentrations of each of the volatile components of interest, is required for the determination of the detector response factors for these components. For maximum accuracy, the calibration standard should be of the same type of emulsion product as the sample being analyzed.

If a "certified" emulsion product, containing known concentrations of the components of interest, is used as the calibration standard, it should be stored in a refrigerator at a temperature below 50 °F to minimize the loss of volatile organic compounds during handling. Even with refrigeration, a standard should not be used if the liquid volume in the container is less than 40% since the volatile organic compounds in the emulsion will have been significantly depleted by transfer into the headspace of the container.

If the standard addition technique is used to prepare the calibration standard, the first step is weigh a 30-gram aliquot of the sample emulsion to be analyzed into a 60 mL Nalgene wide-mouth bottle (or other suitable container), recording the weight to the nearest 0.1 milligrams. To this is added approximately 0.03-0.04 grams each of the two standard mixtures described below in Section V-F. The weights of these additions are also recorded to the nearest 0.1 milligrams. The bottle is then capped and the sample mixture is shaken vigorously for 5 minutes. This material is designated as the "spiked" emulsion standard.

Ideally, the amount of each standard mixture added to the sample emulsion should be sufficient to approximately double the peak areas of the major components of interest over that observed in the initial emulsion. If a component of interest is present at an abnormally high concentration in the sample emulsion, it may be necessary to add a larger amount of the standard mixture.

#### F. Preparation of Standard Mixtures

Two separate standard mixtures are required, one containing the "neutral" components and the other containing the "alcohol" components. It is necessary to prepare two separate solutions to prevent reactions between the alcohol components and the esters. These standard mixtures facilitate the addition of low levels of the volatile organic compounds into the initial emulsion in preparation of the calibration standard described above in Section V-E. The standard mixtures are prepared as described below, recording all weights to the nearest 0.1 milligrams. It should be noted that these weights are only a recommendation and the actual standard composition may be adjusted as the analyst deems necessary.

It is important to note that the compositions of the standard mixtures listed below can be adjusted to suit the analysis that is required. For example, if vinyl acetate is the only component of interest in the

emulsion sample then the "neutrals" mixture would consist only of vinyl acetate and the "alcohols" mixture could be eliminated.

1. "Neutrals" Standard Mixture

Compound	Weight (grams)
acetaldehyde	1.0
pentane	0.1
acetone	1.0
methyl acetate	1.0
vinyl acetate	10.0
ethyl acetate	1.0
methyl acrylate	0.1
methyl ethyl ketone	0.1
n-heptane	0.2
benzene	0.05
methyl cyclohexane	0.2
n-propyl acetate	0.1
1,4-dioxane	0.1
toluene	0.1
n-butyl acetate	0.3
n-butyl acrylate	0.3
<b>TOTAL</b>	<b>15.65</b>

2. "Alcohols" Standard Mixture

Compound	Weight (grams)
methanol	5.0
ethanol	2.0
isopropanol	2.0
t-butanol	1.0
n-propanol	1.0
isobutanol	1.0
n-butanol	1.0
<b>TOTAL</b>	<b>13.0</b>

As stated above, the compositions of the standard mixtures can be adjusted to suit the analysis that is required. The following special cases further illustrate how these mixtures may be "customized" to suit the specific situation at the manufacturing facility.

<u>Emulsion Product</u>	<u>"Neutrals" Mixture</u>	<u>Weight (grams)</u>	<u>"Alcohols" Mixture</u>	<u>Weight (grams)</u>
FL LC-16	acetaldehyde	1.0	ethanol	5.0
	vinyl acetate	8.0	t-butanol	5.0
	1,4-dioxane	1.0		
FL SP-27 and	acetaldehyde	1.0	ethanol	5.0
	vinyl acetate	8.0	t-butanol	5.0
FL GP-33 and FL-SP-18	1,4-dioxane	1.0		

A standard addition technique can not be used for the accurate quantitation of the C<sub>1</sub>-C<sub>4</sub> hydrocarbons. If the hydrocarbons of interest are added in the gas phase to the headspace of an emulsion contained in a sealed vial, a true partitioning into the solid/liquid phase of the emulsion does not occur. The outcome of this is an erroneously low hydrocarbon response factor and subsequent calculation of a lower than actual hydrocarbon concentration in the emulsion sample.

If accurate quantitation of the C<sub>1</sub>-C<sub>4</sub> hydrocarbons is required, a Multiple Headspace Extraction procedure should be followed. Alternatively, the procedure described in Section VI-D, using a pre-determined correction factor, can be applied.

#### G. Calibration Using a "Certified" Emulsion Standard

If the gas chromatograph-headspace system is being calibrated for the first time using a "certified" calibration standard, it is recommended that the analysis be performed in triplicate. First, vigorously shake the emulsion standard to achieve good mixing before removing aliquots for analysis. Weigh three 10 gram aliquots of the emulsion standard into headspace vials. For maximum accuracy the emulsion weight should be within 0.05 gram of the 10 gram target weight. The vial is immediately tightly sealed with an aluminum crimp cap and Teflon-faced silicone septa. (The seal should be sufficiently tight to prevent turning the cap by hand.)

It is recommended that a blank vial containing 10 grams of deionized water be analyzed prior to the emulsion standard. This will provide a "steam-cleaning" of all surfaces within the headspace analyzer which are exposed to the emulsion headspace as well as provide a temperature conditioning step for the capillary column. It also allows the refrigerated emulsion standard additional time to achieve room temperature before equilibration in the headspace analyzer.

All vials will be thermostated at 30 °C for thirty minutes in the Tekmar headspace analyzer (or at 40°C for thirty minutes in the Hewlett-Packard headspace analyzer) prior to injection of a one milliliter aliquot of the vial headspace into the gas chromatograph. The oven temperature program and the data system will be automatically started at the same time that the injection is made.

Identification of each component of interest in the chromatogram of the emulsion standard is based on peak retention time. Typical retention times are listed in Table 1 and a typical chromatogram is illustrated in Figure 1. Absolute detector response factors for each component are calculated using the procedure described below in Section VI-A.

The quality assurance requirements in Section VII require a routine analysis of the calibration standard at least once each operating day. A single analysis is acceptable for this calibration check although a blank vial containing 10 grams of water should be analyzed immediately prior to the emulsion standard. The SQC guidelines listed in Section VII should be followed to determine if the instrument calibration is still in "control". If a calibration update is required, the emulsion standard should be analyzed in triplicate as described above.

#### H. Calibration Using the Standard Addition Technique

First, vigorously shake the emulsion sample to achieve good mixing before removing aliquots for analysis. Two 10 gram aliquots of the "control" or unaltered sample (used for preparation of the "spiked" emulsion standard in Section V-E above) are weighed into headspace vials which are then tightly sealed with an aluminum crimp cap and Teflon-faced silicone septa. (The seal should be sufficiently tight to prevent turning the cap by hand.) Each aliquot should be within 0.05 gram of the 10.00 gram target weight for maximum accuracy.

It is recommended that a blank vial containing 10 grams of deionized water be analyzed prior to the emulsion "control". This will provide a "steam-cleaning" of all surfaces within the headspace analyzer which are exposed to the emulsion headspace as well as provide a temperature conditioning step for the capillary column.

Each vial is thermostated at 30°C for thirty minutes in the Tekmar headspace analyzer (or at 40°C for thirty minutes in the Hewlett-Packard headspace analyzer) immediately prior to injecting a one milliliter aliquot of the vial headspace into the gas chromatograph. The oven temperature program and the data system are started simultaneously at the same time that the injection is made.

Similarly, two 10 gram aliquots of the "spiked" emulsion standard are weighed into headspace vials which are then sealed and analyzed in the same manner as above. Although it is preferable to perform these analyses in duplicate, a single analysis of the "control" and "spiked" emulsions is acceptable if a time constraint exists. It is important to always analyze the "control" vials first to avoid the potential for carryover of any volatile organic compounds from the "spiked" emulsion. It is also good practice to analyze a blank vial containing 10 grams of deionized water after the "spiked" emulsion, prior to the analysis of subsequent emulsion samples.

Identification of each component in the chromatogram is based on retention time. Typical component retention times are listed in Table 1 and a typical chromatogram is illustrated in Figure 1. Absolute detector response factors for each component are calculated using the procedure described below in Sections VI-B and VI-C.

#### I. Sample Preparation and Analysis - Water-Based Polymer Emulsions

The composition of the sample emulsion used for the preparation and analysis of the "control" and "spike" in the procedures described above in Sections V-E and V-H can be determined from the data obtained in Section V-H and using the calculations described below in Sections VI-B through VI-D.

Additional emulsion samples (preferably of the same product) are analyzed by weighing ten grams of the sample emulsion into a headspace vial which is then sealed. The sample temperature should not exceed 85 °F when the sample container is opened to avoid undue loss of the volatile components. Vigorously shake the sample to achieve good mixing before removing the 10 gram aliquot. For maximum accuracy, the sample weight should be within 0.05 grams of the 10 gram target weight.

Thermostat the vial at 30°C for thirty minutes in the Tekmar headspace analyzer (or at 40°C for thirty minutes in the Hewlett-Packard headspace analyzer) prior to injecting a one milliliter aliquot of the vial headspace into the gas chromatograph. Calculate the concentration of each component of interest in the sample using the relationship described in Section VI-D.

#### J. Sample Preparation and Analysis - Redispersible Powders

Spray dry redispersible powders may also be analyzed for VOC by headspace gas chromatography. The first step is to prepare an aqueous solution containing 20 % by weight of the sample powder. Weigh 6.0 grams of the sample into a 60 mL Nalgene wide-mouth bottle (or other suitable container), recording the weight to the nearest 0.1 milligram. To this is added 24.0 grams of deionized water. The bottle is then capped and the sample mixture is shaken vigorously until all the powder has been dissolved/dispersed into solution. This sample mixture is designated as the "control".

A second sample mixture is prepared as above and used for preparation of the calibration standard as described in Section V-E. After the powder has been dissolved/dispersed, add approximately 0.03-0.04 gram each of the two standard mixtures described in Section V-F above. The weights of these additions are recorded to the nearest 0.1 milligram. The bottle is then capped and the sample mixture is shaken vigorously for 5 minutes. This material is designated as the "spiked" standard.

Calibration of the instrument is performed as described above in Section V-H and the sample composition is calculated as described below in Sections VI-B through VI-D.

## VI. CALCULATIONS

### A. Calculation of Detector Response Factor ("Certified" Emulsion Standard)

The data obtained in Section V-G from the analysis of the "certified" emulsion standard are used to calculate absolute detector response factors for each component of interest using the following relationship:

$$RF_N = \frac{C_N}{A_N} \quad (1)$$

where:

- $RF_N$  = Absolute detector response factor for component N (wt ppm per area)
- $A_N$  = Peak area of component N
- $C_N$  = Concentration (wt ppm) of component N in the "certified" emulsion standard

For example, the vinyl acetate peak in the "certified" emulsion standard (820 wt ppm vinyl acetate) has 463,800 area counts. The response factor for vinyl acetate is determined to be  $1.7680 \times 10^{-3}$  using the relationship described above.

$$RF_{VAM} = \frac{820}{463,800} = 1.7680 \times 10^{-3}$$

Since absolute detector response factors are extremely dependent on the instrumental system, it is necessary to redetermine the response factors after any modifications have been made to the operating parameters.

### B. Calculation of Component Concentrations Added to the Initial Emulsion (Standard Addition)

If a standard addition procedure is used to prepare the calibration standard, then the first step is to calculate the fraction of each component in the "neutrals" and "alcohols" standard mixtures using the following relationship:

$$F_N = \frac{W_N}{W_T} \quad (2)$$

where:

- $F_N$  = Fraction of component N in the standard mixture (Section V-F)
- $W_N$  = Weight in grams of component N in the standard mixture
- $W_T$  = Total weight in grams of the standard mixture

Next, calculate the concentration of each component added into the initial emulsion in preparation of the "spiked" emulsion standard using the relationship:

$$C_N = \frac{W_S \times F_N}{W_T + W_E} \times 10^6 \quad (3)$$

where:

- $C_N$  = Concentration (wt ppm) of component N which has been added in preparation of the "spiked" emulsion standard
- $W_S$  = Weight in grams of the "neutrals" or "alcohols" standard mixture added to the emulsion
- $F_N$  = Fraction of component N in that standard mixture
- $W_T$  = Total weight of both the "neutrals" and "alcohols" standard mixtures added to the emulsion
- $W_E$  = Weight in grams of the emulsion (for the redispersible powders, this is the total of the weight of the water plus the weight of the powder)

For example, the "alcohols" standard mixture contains 5.0727 grams of methanol in a total of 13.1775 grams of solution. The addition of 0.0348 grams of the "alcohols" standard mixture (and 0.0356 grams of the "neutrals" standard mixture) to 30.6801 grams of emulsions yields an additional methanol concentration of 435.7 wt ppm.

$$F_{\text{MeOH}} = \frac{5.0727}{13.1775} = 0.3850$$

$$C_{\text{MeOH}} = \frac{0.0348 \times 0.3850}{0.0704 + 30.6801} \times 10^6 = 435.7 \text{ wt ppm added}$$

### C. Calculation of Detector Response Factor (Standard Addition)

The data obtained in Section V-H from the analysis of the "control" emulsion and the "spiked" emulsion standard are used to calculate absolute detector response factors for each component of interest.

Following the determination of the component concentration added to the initial emulsion, this "spiked" emulsion material may be used as a calibration standard to calculate the absolute detector response factor for each component as follows:

$$RF_N = \frac{C_N}{\Delta A_N} \quad (4)$$

where:

- $RF_N$  = Absolute detector response factor for component N (wt ppm per area)
- $\Delta A_N$  = Difference in area counts between the initial "control" emulsion and the "spiked" emulsion standard for component N
- $C_N$  = Concentration (wt ppm) of component N which was added in preparation of the "spiked" emulsion (as calculated in Section VI-B)

For example, the methanol peak in the "spiked" emulsion (435.7 wt ppm additional methanol added) has 36,120 area counts and the "control" emulsion has 11,490 area counts for methanol. The response factor for methanol is determined to be  $1.7690 \times 10^{-2}$  using the relationship described above.

$$RF_{\text{MeOH}} = \frac{435.7}{(36,120 - 11,490)} = 1.7690 \times 10^{-2}$$

Since absolute detector response factors are extremely dependent on the instrumental system, it is necessary to redetermine the response factors after any modifications have been made to the operating parameters.

All of the calculations described above in Sections VI-B and VI-C can be easily performed using a spreadsheet in Excel™ or similar software. This format can also be applied to the calculations described below in Section VI-D for determination of sample composition.

#### D. Calculation of Sample Composition (Water-Based Polymer Emulsions)

The concentration of each component in an emulsion sample is calculated using the following relationship:

$$C_N = A_N \times RF_N \quad (5)$$

where:

- $C_N$  = Concentration (wt ppm) of component N in the original sample
- $A_N$  = Peak area of component N
- $RF_N$  = Absolute detector response factor for component N

For example, using the response factor for vinyl acetate ( $1.7680 \times 10^{-3}$ ) determined above in Section VI-A, a sample of emulsion containing 294,300 area counts for the vinyl acetate peak has a vinyl acetate concentration of 467 wt ppm.

$$C_{\text{MeOH}} = 294,300 \times 1.7680 \times 10^{-3} = 467 \text{ wt ppm}$$

Any uncalibrated and/or unidentified components can be quantified using the ethyl acetate response factor and summed under the designation of "others". The sum of all component concentrations plus these "others" provides a Total Volatile Organic Compound (TVOC) value for the sample.

An alternative procedure for obtaining a TVOC value is to quantify only the major components using the above procedures and add a statistically-determined factor whose value represents the concentrations of all other components which may be present. This procedure can currently be applied only to the products listed below which are manufactured at the Piedmont (SC) facility.

<u>Emulsion Product</u>	<u>Quantified Components</u>	<u>TVOC factor (wt ppm)</u>
FL LC-16	acetaldehyde vinyl acetate 1,4-dioxane	681
FL SP-27	acetaldehyde vinyl acetate 1,4-dioxane	359
FL GP-33	acetaldehyde vinyl acetate 1,4-dioxane	176

In some instances, not all identifiable components in the sample are of interest. In this case, only the components of interest are reported and all others are merely summed and reported as "others". With the exception of those products listed above, determination of a valid TVOC value requires that all components present in the sample headspace be quantified, either by using the response factor determined for each component or by using the ethyl acetate response factor.

Quantitation of the C<sub>1</sub>-C<sub>4</sub> hydrocarbons can be obtained by using the response factor for vinyl acetate and multiplying the resulting concentration by a correction factor of  $1.7511 \times 10^{-3}$ . This correction factor has been determined for ethylene using a Multiple Headspace Extraction (MHE) procedure. Application of this factor to the other hydrocarbons provides a convenient means of obtaining a reasonable accurate value for the concentration.

It is assumed in this method that the partitioning of analytes in the sample headspace is identical to that for the calibration standard, independent of any matrix effects. For maximum accuracy, therefore, it is recommended that the "control" and "spiked" emulsions used for the instrument calibration be of the same type of emulsion as the sample being analyzed. This is particularly important if the sample viscosity is widely different. It should also be noted that although the sample weight is not used in the determination of component concentration, in order to obtain maximum accuracy of this method, the weight of the sample should be between 9.95 and 10.05 grams (within 0.05 grams of the 10.00 gram target weight).

#### E. Correction of Vinyl Acetate Concentration for Difference in Sample Type

As stated above, maximum accuracy of this analysis is obtained if the emulsion standard and emulsion sample are of the same type or product line. If a "certified" emulsion standard is used for calibration, it is highly possible that the emulsion sample may be of a widely different type than the standard. In this case, the concentration calculated above in Equation 5 will need to be multiplied by a correction factor to obtain a more accurate value, as illustrated below. This correction applies only to the determination of vinyl acetate concentration in a limited number of emulsion products. A listing of emulsion products and correction factors is attached in Table 2.

The corrected concentration of vinyl acetate in an emulsion sample is calculated using the following relationship:

$$C_N = A_N \times RF_N \times RRF_N \quad (6)$$

where:

- $C_N$  = Concentration (wt ppm) of vinyl acetate in the original sample
- $A_N$  = Peak area of vinyl acetate
- $RF_N$  = Absolute detector response factor for vinyl acetate
- $RRF_N$  = Relative response factor for specific emulsion product versus the calibration standard (see Table 2)

For example, using the response factor for vinyl acetate calculated above in Section VI-A using a "certified" emulsion standard of A-320, a sample of A-465 emulsion containing 535,200 area counts for the vinyl acetate peak has a concentration of 1183 wt ppm vinyl acetate.

$$C_{VAM} = 535,200 \times 1.7680 \times 10^{-3} \times 1.25 = 1183 \text{ wt ppm}$$



## F. Calculation of Sample Composition (Redispersible Powders)

The concentration of each component in a sample of redispersible powder is calculated using the following relationship:

$$C_N = A_N \times RF_N \times DF \quad (7)$$

where:

$C_N$  = Concentration (wt ppm) of component N in the original sample  
 $A_N$  = Peak area of component N  
 $RF_N$  = Absolute detector response factor for component N  
 $DF$  = Dilution Factor

The Dilution Factor is calculated using the following relationship:

$$DF = \frac{W_{\text{powder}} + W_{\text{water}}}{W_{\text{powder}}} \quad (8)$$

where:

$DF$  = Dilution Factor  
 $W_{\text{powder}}$  = Weight in grams of the redispersible powder used in preparing the aqueous mixture  
 $W_{\text{water}}$  = Weight in gram of water used in preparing the aqueous mixture

For example, a 6.0500 gram aliquot of redispersible powder was mixed with 24.1050 grams of deionized water to provide an aqueous dispersion. Analysis of this mixture provided a peak area of 2,470 for methanol. Using the response factor for methanol determined above in Section VI-C, a methanol concentration of 218 wt ppm is calculated.

$$C_{\text{MeOH}} = 2,470 \times 1.7690 \times 10^{-2} \times (6.0500 + 24.1050)/6.0500 = 218 \text{ wt ppm}$$

## PRECISION AND ACCURACY

### A. Precision

The precision of this method was determined by analyzing a "spiked" emulsion in triplicate. The concentrations of the various components (listed in Section I) ranged from 2 to 2000 wt ppm and the percent relative standard deviation (%RSD) ranged from 0.1 to 3%. The average %RSD for all components was approximately 1.0%.

### B. Accuracy

To determine the accuracy of the method, the amount of each component present in both a "spiked" emulsion and a "control" emulsion was calculated. The difference in concentration between the "spiked" emulsion and the "control" emulsion was compared to the actual amount added in preparing the "spiked" emulsion. From this information, the percent recovery for each component was calculated using the relationship:

$$\text{Percent Recovery} = \frac{\text{calculated difference}}{\text{actual spiked amount}} \times 100$$

The actual concentrations of the various components (listed in Section I) ranged from 2 to 2000 wt ppm and the percent recoveries ranged from 72 to 110%. The average percent recovery for all components was approximately 92%.

### C. Reporting Precision

The precision of the analysis for each sample is reported when multiple determinations are made. The statistical information includes the mean (average) value of the determinations ( $\bar{X}$ ), the standard deviation of the determinations ( $S$ ), and the number of replicate determinations ( $n$ ). The standard deviation is calculated using the relationship:

$$S = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n - 1}} \quad \text{where } X_i \text{ is the value of the individual determination.}$$

The recommended format for reporting the above statistical information is  $\bar{X} (S, n)$ .

## VIII. QUALITY ASSURANCE

The chromatographic instrumentation should be maintained according to the instrument manufacturer's recommendations.

An instrument malfunction is often evidenced by changes, either gradual or sudden, in the peak retention times. The retention times of the peaks of interest should be monitored continuously. Gradual or sudden shifts in the area counts observed for the standard components are another indication of a malfunctioning instrument. Any variations judged to be significant to the chromatographer should be investigated by checking the chromatographic conditions and supporting equipment.

Even though an instrument appears to be functioning properly (reproducible retention times and peak areas), it is advisable to monitor the consistency of the instrumentation by analyzing a calibration standard daily. It is good practice to calculate the absolute detector response factor for vinyl acetate (or other component of interest) as described above and maintain a record of these values, such as in a control chart or other appropriate SQC procedure.

### SAFETY

Operations involving the handling of all chemicals should be done in a well ventilated hood. Chemically resistant gloves, such as disposable nitrile gloves, and proper protective clothing should be worn when handling chemicals to prevent contact with the skin. Decontaminate skin with soap and water immediately if contacted.

### REFERENCES

Analytical Procedure CRSD-008-91, "Gas Chromatographic Method for the Determination of Residual Vinyl Acetate Monomer (VAM)"

Analytical Procedure 93-CRSD-038, "Headspace Gas Chromatographic Method for the Analysis of Residual Vinyl Acetate Monomer (VAM) and Vinyl Chloride Monomer (VCM) in Emulsions"

Analytical Procedure 93-CRSD-038, Revision 1, "Headspace Gas Chromatographic Method for the Analysis of Residual Vinyl Acetate Monomer (VAM) and Vinyl Chloride Monomer (VCM) in Emulsions"

Analytical Procedure 93-CRSD-048, "Headspace Gas Chromatographic Method for the Analysis of Residual Volatile Organic Compounds (VOC) in Emulsions"

**Table 1**  
**Representative Retention Times**

<b><u>Component</u></b>	<b><u>Retention Time</u> <u>(minutes)</u></b>
methane	5.11
ethane/ethylene	5.20
propane/propylene	5.49
isobutylene	6.16
vinyl chloride	6.32
acetaldehyde	7.01
methanol	7.39
pentane	7.57
ethanol	8.93
acetone	9.87
isopropanol	9.96
methyl acetate	10.11
t-butanol / trans-2-methyl hexene	10.69
vinyl acetate	11.77
n-propanol / 2-methyl hexane	12.35
ethyl acetate	12.93
methyl acrylate	13.20
methyl ethyl ketone	13.43
methyl propionate (propanoate)	13.58
n-heptane	13.67
benzene / isopropyl acetate	14.58
isobutanol	14.87
methyl cyclohexane	15.30
n-butanol / ethyl acrylate / crotonaldehyde	16.26
n-propyl acetate / methyl methacrylate	16.73
1,4-dioxane	17.22
toluene	18.81
methyl isobutyl ketone	18.88
n-butyl acetate	20.67
n-butyl acrylate	23.83
styrene	24.22
alpha-methyl styrene	27.20

**Table 2**  
**Vinyl Acetate Relative Response Factors (RRF<sub>N</sub>) for Emulsion Products**

Emulsion Product used as Calibration Standard

Sample	A-320	XX-220	A-738
A-100HS	0.89		
A-105	0.88		
A-108	0.91		
A-124	0.86		
A-129	0.82		
A-175	0.726		
A-181	0.847		
A-300	0.99		
A-320	1.00		
A-323	1.00		
A-400	0.99		
A-400H	1.01		
A-401	1.06		
A-410	1.01		
A-426	1.03		
A-465	1.25		
A-500	0.92		
A-510	0.95		
A-560BP	0.92		
A-600BP	0.81		
A-728	0.64		1.00
A-920	0.85		
A-1630	0.96		
A-4500	0.55		0.86
A-4514	0.44		0.69
A-4530	0.51		0.80
A-7200	1.223		
CA-52	1.07		
F-149	0.74	0.78	
F-150	0.72	0.76	
F-325	0.90	0.95	
F-345	0.86	0.91	
F-380	0.97	1.02	
RB-8	0.95		
V-810L	0.63	0.66	
V-881	0.73	0.77	
V-882M	0.71	0.75	
V-884	0.70	0.74	
V-1000	0.77	0.81	
XX-210	0.86	0.91	
XX-220	0.95	1.00	
XX-230	0.94	0.99	
XX-240	0.93	0.98	

**Figure 1      "Spiked" Emulsion Standard**